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VITREOUS COATING

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1 Claim. (Cl. 106—48)

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This application is a continuation in part of applications filed by me July 28, 1938, Serial No. 221,793, now abandoned, and February 17, 1940, Serial No. 319,517, now abandoned.

In the production of enamel ware, that is to say metal (typically sheet steel) coated with vitreous enamel fused upon its surface, an imperfection is likely to occur that is known as hair-lining or tearing. In the finished article dark lines are apt to appear, lines where there has been a break in the continuity of the coating material, with the effect that underlying material shows through. This is of importance, particularly in white or light-colored enamel ware.

I have made considerable investigation and have perceived the causes of the defect, and my invention lies in the discovery of preventive means.

In typical procedure the article of sheet steel is coated first with a ground coat and fired, and then the ground-coated article is coated with a slip or sprayed-on coating of fluid enamel. This fluid enamel is a dispersion in liquid (ordinarily water) of very fine ground vitreous material, together with (I speak of white enamel) an opacifying material, typically tin oxide. Additionally, about 7% of clay is used as a suspending agent in preparing the slip.

Procedure consists first in coating the article with the slip, then drying, leaving the coating in hard and caked condition upon the surface, and finally firing. In the firing the vitreous material fuses, and in fused condition becomes permanently adherent to the surface.

In the drying of the spread slip and in the handling and in the initial stages of firing, some warping of the steel body is almost unavoidable, and in consequence of warping the caked coating cracks, and the cracks so developed persist in the flaw that is known as hair-lining.

Fineness of grinding of the frit is desirable, in that maturing temperature is lowered, superior surface gloss is attained, and, in the case of opaque enamel, opacity is increased; it has, however, been found that fineness of grinding tends to make more pronounced the defect of tearing or hair-lining, and, accordingly, it has heretofore been found practically necessary to limit

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fineness of grinding to the point at which, if 50 cc. of the milled enamel (=approximately 80-95 grams) be washed through a screen of 200 meshes to the inch, there will remain on the screen a residue of 8-12 grams of the enamel.

It also is desirable that the slip spread upon the surface of the article be, within the limits in contemplation, of maximum thickness; but it has been found that, as thickness increases, the tendency to tearing increases; so that, in consequence, slip thickness is in practice limited to a weight of ground frit of about 35 grams to the square foot.

It is in the provision of cover-coats in the production of enameled steel articles that the difficulty of hair-lining arises. The frit for such coats should be so compounded as to mature at a temperature of 1600° F. or less. An important ingredient of the frits for this purpose is borax. Borax being present, lowers the temperature at which the frit matures to form the cover coat. In the course of grinding of the frit components to produce a mix of the desired degree of fineness, the borax tends to leach out. The finer the grinding and the higher the temperature of the material when subject to the grinding operation, the greater is the leaching effect upon the borax. The borax so leaching into the mill liquor has the effect that the frit when fired tends to hair-line. This tendency is aggravated by increase in the thickness of the applied coating, and, of course, by thermal expansion and contraction of the article after coating and before firing. If an enamel is so compounded that the leaching of the borax is reduced beyond a certain value, hair-lining does not occur.

It is known that the solubility of borax is influenced by the presence of silica and alumina (alumina is introduced into the frit composition in association with silica in the form of feldspar); and if these two constituents, silica and feldspar, be present in the frit in combined quantity not substantially exceeding 50% of the whole, and if borax be present in quantity (as the art knows) sufficient to bring the maturing temperature to 1600° F. or less, the enamel may be made subject to my invention.

My discovery is that if to a frit of the composition and character indicated a particular substance be added, the frit may be ground more finely and the slip may be applied in a coating of greater thickness, and yet the defect of hair-lining will not ensue. The substance added is a material of relatively low melting point, typically sodium nitrite (a compound that melts at about 520° F.). The sodium nitrite is added in amount varying from 0.125% to 1% by weight of the frit. It is intimately mingled with the finely divided glass, and is preferably, though not necessarily, combined with the glass before the glass is ground with water to the condition of a slip. It may, however, be added, dissolved in water, to the already milled slip. It is itself water-soluble and in the slip, however it be added, it comes to dissolved state. When the article has been coated with material that carries such sodium-nitrite content and is at the beginning of the firing operation, the early fusion of the sodium nitrite effects such an early adhesion of the coating to the underlying surface that the cleavages productive of hair lines either do not occur or, having occurred, do not develop, and the coating is found to be continuous, and the product free of the cracks under consideration.

In the firing of coats of enamel that are compounded as usual and lack the modification in which my present invention is found, the coating in the early stages of firing becomes crazed with a network of fine fissures. These tend to intensify the fissures that endure as hair-lines. In the firing of a coating of my invention such crazing in the initial stages of firing does not occur.

I have found that, if I make such an addition of sodium nitrite, the grinding of the frit may be carried farther, and with the recognized advantages of so doing, and yet without suffering the countervailing liability of the enamel to tearing or hair-lining. I have found that, with the aid of the sodium nitrite addition, a frit ground to a fineness more minute than that defined above will, when worked to a slip and applied, still be serviceable and free of the defect of hair lining; I have found that the frit may be ground to such degree of fineness that it will pass substantially in toto through a 200-mesh screen, and yet tearing or hair-lining will not develop. I have further found that with the sodium nitrite addition the slip may be applied in a coating as thick as 40-70 grams of frit to the square foot, and yet the fired article will be free of hair-lining.

Incidentally, in the firing of ground coats upon articles of steel, the presence of nitrite of sodium in the ground coat (producing fusion at lower temperature) tends to give a better union of the coating to the metal, that is to say, the bonding effect is improved, in that it permits of wider deviations from normal practice without detriment.

When an article of steel, upon whose surface lies a hardened coating of usual composition, is introduced into the furnace and fired, as the temperature mounts, air, gaining access through the porous coating, produces iron oxide at the metal-coating interface. In the practice of my invention the fusion at relatively low temperatures of the sodium nitrite content of the coating has effect in sealing the steel surface from access of air, and so in diminishing the extent of such oxidation.

The following are exemplary formulae for frit

upon which my invention may with success be practiced:

Clear enamel

	Per cent
5 Silica -----	20.15
Titanium oxide -----	3.70
Soda ash -----	6.10
Cryolite -----	5.55
Dehydrated borax -----	16.00
10 Fluorspar -----	4.63
Zinc oxide -----	3.70
Nitrate of soda -----	4.62
Feldspar -----	30.43
Whiting -----	1.42
15 Sodium silico-fluoride -----	3.70
Total -----	100.00

Opacified enamel

	Per cent
20 Silica -----	18.59
Titanium oxide -----	1.86
Soda ash -----	4.18
Cryolite -----	7.06
Dehydrated borax -----	16.02
25 Fluorspar -----	11.70
Nitrate of soda -----	6.60
Feldspar -----	23.59
Barium carbonate -----	2.41
30 Antimony trioxide -----	7.99
Total -----	100.00

In each of these cases, if to the frit nitrite of sodium be added in the quantity specified, hair-lining, to which the applied enamel would otherwise be liable, will not occur.

The modifying material must meet certain conditions: it must be of low melting point (not exceeding and preferably lower than 1000° F.); it must be chemically inert, to this extent, that at its own melting point it will not react with the glass, nor with the metal of the article being coated; and it must have neither disfiguring nor discoloring effect. To meet these requisites a wide range of particular materials is available. So far as I have investigated, no elemental substance will serve; but there are many compounds that will serve. For practical purposes metallic salts are most readily available, and I specify particularly, in addition to sodium nitrite, potassium sulphocyanide, whose melting point is about 343° F., other alkali-metal sulphocyanides, and alkali-metal salts of low melting point generally, and stannous chloride, with a melting point of about 447° F. In all of these cases the quantity will be within the range specified above for sodium nitrite (0.125-1.00%).

The invention, developed in the enamel-ware industry, is of general applicability in the formation of vitreous coatings upon bodies of various substances, both metallic (cast iron, for example) and non-metallic (pottery, for example).

I believe that I am the first to discover the value of sodium nitrite and the equivalent substances specified, in the manner and under the circumstances described and with the effect of preventing tearing or hair-lining.

I claim as my invention:

A slip for the enameling of a steel article, formed from a frit that includes feldspar and silica in combined quantity not substantially exceeding 50% and that includes also a borax, and of a maturing temperature not exceeding 1600° F., fortified against tearing by the inclusion of a salt of an alkali metal having a melting point

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not exceeding 1000° F., the salt of the alkali metal employed being a sulpho-cyanide and the quantity being 0.125-1.00%.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,010,776	Frost	Aug. 6, 1935
2,250,456	Bahnsen et al.	July 29, 1941
2,250,457	Bahnsen et al.	July 29, 1941

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FOREIGN PATENTS

Number	Country	Date
297,725	Great Britain	1929
643,805	Germany	1937

OTHER REFERENCES

Andrews: Enamels, pages 260, 378, 379 (1935).
Journal American Ceramic Society: "The
Tearing of Vitreous Enamels," by Rosenberg &
Langerman, vol. 23 (3) 83-86, March 1940.